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(54) **Corrosion-inhibited antifreeze/coolant composition.**

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GB-A- 2 122 598
US-A- 2 832 742
US-A- 4 382 008
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Description

This invention relates to a metalcorrosion inhibitor for use in aqueous solutions, and to antifreeze/coolant compositions containing such a corrosion inhibitor. More particularly, this invention relates to corrosion-inhibited aqueous and antifreeze/coolant compostions comprising a combination of alkylbenzoic and aliphatic monobasic acids and/or the alkali metal, ammonium, or amine salts of said acids.

Automobile engine cooling systems contain a variety of metals, including copper, solder, brass, steel, cast iron, aluminium, magnesium, and their alloys. The possibility of corrosive attack on such metals is high, due to the presence of various ions as well as the high temperatures, pressures, and flow rates found in such cooling systems. The presence of corrosion products within the cooling system can interfere with heat transfer from the engine combustion chambers, which may subsequently cause engine overheating and engine component failure due to excess metal temperatures. See generally Fay, R. H., "Antifreezes and Deicing Fluids," In: Kirk-Othmer Encyclopedia of Chemical Technology (1978) ed.), vol. 3, pp. 79 - 95. It would therefore be generally advantageous if the formation of corrosion products within automobile cooling systems could be controlled or eliminated. It is one object of the instant invention to provide a corrosion inhibitor useful in the prevention and control of corrosion in automobile engine cooling systems containing various metals.

The trend towards improved fuel economy for automobiles has led to the increased use of lightweight materials such as aluminum and magnesium alloys for engine and cooling system components. However, it has been found that pitting and crevice corrosion are particularly prevalent in aluminum-containing cooling systems. Pitting of thin-walled automobile radiator tubes may lead to tube perforation; crevice corrosion at cylinder head packings or coolant hose connections may also occur. Both types of corrosion may lead to eventual coolant loss, with subsequent engine overheating and component failure. Other forms of localized corrosion such as deposit attack from deposition of corrosion products may also result.

Many conventional corrosion inhibitor additives used in automobile cooling systems do not provide adequate protection against the pitting, crevice, and deposit attack corrosion phenomena found with aluminum and various other metal alloys. It would therefore be particularly advantageous if such localized corrosion phenomena could be controlled or eliminated. If is another object of the instant invention to provide a corrosion inhibitor for use in automobile cooling systems which prevents or controls localized corrosion of aluminum, magnesium, and various other metal surfaces.

All corrosion inhibitors employed in automobile antifreeze/coolant formulations are gradually depleted by use and the build-up of corrosion products in the cooling system. It would thus be advantageous if the build-up of corrosion products within the system and subsequent corrosion inhibitor depletion or degradation could be controlled or eliminated. It is a further object of the instant invention to provide a corrosion inhibitor which is less prone to depletion or degradation than traditional corrosion inhibitors used in antifreeze/coolant formulations.

It is well known that various monobasic and dibasic acids as well as the salts of such acids are effective as corrosion inhibitors when employed in antifreeze/coolant formulations.

The general use of alkylbenzoic acids/salts as corrosion inhibitors is well known. For example, U.S. Pat. Nos. 4,501,667, 4,402,907 and 4,366,076 disclose that alkylbenzoic acids such as 4-tert-butylbenzoic acid are useful as metal corrosion ibhibitors. In addition:

U.S. Pat. No. 4,552,678 discloses a corrosion inhibitor obtained from the reaction product of a polyamine, an anhydride, and an organic acid of the formula R_2 - COOH where R_2 may be H, a C_1-C_{12} alkyl C_1-C_5 hydroxyalkyl, phenyl, tert-butyl, phenyl, or styryl radical;

U.S. Pat. No. 3,769,214 discloses an aqueous lubricant composition containing a minor amount of a metal anti-staining agent and stability improver which is an alkanolamine salt of a carboxylic acid having at least 12 carbon atoms per molecule;

U.S. Pat. No. 2,832,742 discloses the use of a blend of the diethanol amine salts of p-tert-butylbenzoic acid and a high molecular weight C_7-C_{18} aliphatic carboxylic acid mixture derived from an oxidized petroleum fraction;

Japanese Pat. No. 59208082 discloses a method of inhibiting corrosion in a cooling water system for an internal combustion engine via addition of a corrosion inhibitor containing a water soluble amine salt of benzotriazole, a water soluble amine salt of t-butylbenzoic acid, a nitrite, and a benzoate to the cooling water;

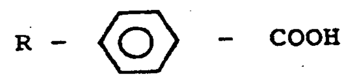
API Primary Petroleum Products Abstract No. 76-20709 describes French Pat. No. 2268791, which discloses a water soluble ferrous metal corrosion inhibitor which is the condensation product of a C_1-C_6 para-alkylbenzoic acid and an alkanolamine.

Japanese Patent No. 035676 describes a corrosion inhibitor comprising a benzoic acid derivative, a hydrocarbyl triazole and a phosphoric acid or salt thereof. US-A-2832742 provides a corrosion inhibitor for cooling systems containing ethylene glycol, which inhibitor comprises a blend of equal parts of butyl benzoic acid with

a C_7 - C_{18} aliphatic carboxylic acid neutralized by a reaction with an organic amine.

The present invention relates to improvements in inhibitors of this type including 90 to 99 wt % of a water soluble liquid alcohol freezing point depressant,
characterised by

a) from 0.1 to 5.0 wt % of an alkylbenzoic acid or an alkali metalm ammonium, or amine salt thereof, said acid having the general formula



where R is a C_1 - C_5 alkyl radical;

b) from 0.1 to 5.0 wt % of a c_8 - C_{12} aliphatic monobasic acid or an alkali metalm ammonium, or amine salt thereof; and

c) from 0.1 to 0.5 wt % of a hydrocarbyl triazole.

The most preferred corrosion inhibitor of the instant invention comprises: the alkylbenzoic acid 4-tert-butylbenzoic acid, or the alkali metal, ammonium, or amine salt thereof; the aliphatic monobasic acid octanoic acid or 2-ethylhexanoic acid or the alkali metal, ammonium, or amine salts thereof; and the hydrocarbyl aromatic triazole tolyltriazole.

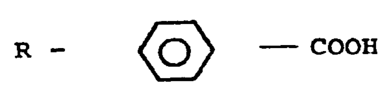
Additional corrosion inhibitors which may be employed in admixture with the novel corrosion inhibitor of the instant invention include: corrosion inhibitors selected from alkali metal borates, alkali metal silicates, alkali metal benzoates, alkali metal nitrates, alkali metal nitrites, alkali metal molybdates, and hydrocarbyl thiazoles; and C_8-C_{12} aliphatic dibasic acids, or the alkali metal, ammonium, or amine salts thereof, preferably sebacic acid or the alkali metal, ammonium, or amine salt thereof.

Aqueous compositions containing said corrosion inhibitor as well as liquid alcohol based antifreeze/coolant formulations containing said corrosion inhibitor are also described. Compositions containing the corrosion inhibitor of the instant invention exhibit a synergistic resistance to corrosion in comparison with compositions containing either the alkylbenzoic or aliphatic monobasic acid/salt component above.

DETAILED EMBODIMENTS OF THE INVENTION

The novel corrosion inhibitor of the instant invention comprises the combination of an alkylbenzoic acid and aliphatic monobasic acid and/or the alkali metal ammonium, or amine salts of such acids, together with a hydrocarbyl triazole, for use in aqueous systems and in antifreeze/coolant concentrate and aqueous antifreeze/coolant formulations.

The alkylbenzoic acid component of the corrosion inhibitor is of the general formula



where R is a C_1-C_5 alkyl radical. 4-tert-butylbenzoic acid (hereinafter referred to as PTBBA) is the most preferred alkylbenzoic acid for use in the instant invention. Alkali metal, ammonium, or amine salts of the alkylbenzoic acid may also be employed. Any alkali metal, ammonium, or amine may be used to form the alkylbenzoic acid salt; however, alkali metals are preferred. The most preferred alkali metals for use are sodium and potassium.

The aliphatic monobasic acid component of the corrosion inhibitor may be any C_8-C_{12} aliphatic monobasic acid or the alkali metal, ammonium, or amine salt of said acid. This would include one or more of the following acids or isomers thereof: octanoic, nonanoic, decanoic, undecanoic, dodecanoic, and 2-ethylhexanoic and mixtures thereof. Octanoic acid (hereinafter referred to as OA) and 2-ethylhexanoic acid (hereinafter referred to as EHA) are particularly preferred. Any alkali metal, ammonium, or amine can be used to form the monobasic acid salt; however, alkali metals are preferred. Sodium and potassium are the preferred alkali metals for use in forming the monobasic acid salt.

The hydrocarbyl triazole component of the corrosion inhibitor of the instant invention is preferably an aromatic triazole or alkyl-substituted aromatic triazole such as benzotriazole or tolytriazole. The most preferred hydrocarbyl triazole for use is tolyltriazole (hereinafter referred to as TTZ).

One or more conventional corrosion inhibitors may also be employed in admixture with the novel corrosion inhibitor of the instant invention. Such conventional corrosion inhibitors may be selected from the group comprising: alkali metal borates, alkali metal silicates, alkali metal benzoates, alkali metal nitrates, alkali metal nit-

rites, alkali metal molybdates, and hydrocarbyl thiazoles.

An additional corrosion inhibitor which may optionally be employed in admixture with the corrosion inhibitor of the instant invention is a C_8-C_{12} aliphatic dibasic acid or the alkali metal, ammonium, or amine salt of said acid. This would include one or more of the following acids: suberic, azelaic, sebacic, undecanedioic, dodecanedioic, the diacid of dicyclopentadiene (hereinafter referred to as DCPDDA), therephthalic, and mixtures thereof. Sebacic acid (hereinafter referred to as SA) is particularly preferred. Any alkali metal, ammonium, or amine may be used to form the dibasic acid salt; however, alkali metals are preferred. Sodium and potassium are the preferred alkali metals for use in forming the dibasic acid salt.

The corrosion inhibitor of the instant invention will most typically be employed in antifreeze formulations as coolants for internal combustion engines. Other applications may include hydraulic fluids, aqueous cutting oils, paints, soluble oils, metal cutting fluids, aircraft deicers, and greases. In these applications, the monobasic and dibasic acid salts may be formed with metal hydroxides including sodium, potassium, lithium, barium, calcium, and magnesium.

In one embodiment of the instant invention, the above-described corrosion-inhibitor is employed in admixture with water to form a corrosion-inhibited aqueous composition. The aqueous composition comprises: a major amount of water; from 0.1-15.0, preferably 0.1-5.0 weight percent of the above-described alkylbenzoic acid/salt corrosion inhibitor component, preferably PTBBA; from 0.1-15.0, preferably 0.1-5.0 weight percent of the above-described aliphatic monobasic acid/salt corrosion inhibitor, preferably OA or EHA; and from 0.1-0.5, preferably 0.1-0.3 weight percent of the above-described hydrocarbyl triazole component, preferably TTZ.

In a preferred embodiment of the instant invention, the above-described corrosion inhibitor is employed in admixture with a liquid alcohol freezing point depressant to from a novel antifreeze/coolant concentrate composition for use in the cooling systems of internal combustion engines. The antifreeze/coolant concentrate composition comprises: from 89-99, preferably 90-99 weight percent of a water soluble liquid alcohol freezing point depressant; from 0.1-15.0, preferably 0.1-5.0 weight percent of the above-described alkylbenzoic acid/salt corrosion inhibitor component, preferably PTBBA; from 0.1-15.0, preferably 0.1-5.0 weight percent of the above-described aliphatic monobasic acid/salt corrosion inhibitor component, preferably OA or EHA; and from 0.1-0.5, preferably 0.1-0.3 weight percent of the above-described hydrocarbyl triazole component, preferably TTZ.

The liquid alcohol freezing point depressant component of the above-described antifreeze/coolant concentrate composition may be a glycol or glycol ether. The glycol ethers which may be employed as major components in the instant invention include glycols such as ethylene glycol, diethylene glycol, propylene glycol, dipropylene glycol, and glycol monoethers such as the methyl, ethyl, propyl, and butyl ethers of ethylene glycol, diethylene glycol, propylene glycol, and dipropylene glycol. Ethylene glycol is particularly preferred as the liquid alcohol freezing point depressant component.

In the above-described antifreeze/coolant concentrate composition of the instant invention, an additional aliphatic dibasic acid/salt corrosion inhibitor, preferably SA, may be employed at concentrations of 0.1-5.0 weight percent. Additional conventional corrosion inhibitors such as alkali metal borates, silicates, benzoates, nitrates, nitrites, molybdates, or hydrocarbyl thiazoles may also be employed at concentrations of 0.01-5.0 weight percent.

In another embodiment of the instant invention, the above-described corrosion-inhibited antifreeze/coolant concentrate composition is diluted with 10-90 volume percent, preferably 25-75 volume percent of water.

The method of the invention will be further illustrated by the following examples, which are not intented limit the invention, but rather to illuminate it.

EXAMPLE 1 (Comparative Example)

A borax-benzoate type antifreeze formulation was prepared comprising a major amount of ethylene glycol, 3.0 weight percent sodium benzoate, 1.0 weight percent borax, 0.2 weight percent sodium metasilicate pentahydrate, 0.2 weight percent sodium nitrate, 0.1 weight percent sodium nitrite, and 0.2 weight percent TTZ.

EXAMPLE 2 (Comparative Example)

An antifreeze formulation was prepared comprising a major amount of ethylene glycol, 3.5 weight percent SA, and 0.2 weight percent TTZ.

EXAMPLE 3 (Comparative Example)

An antifreeze formulation was prepared comprising a major amount of ethylene glycol, 1.75-2.0 weight percent OA, 1.75 weight percent SA, and 0.2 weight percent TTZ.

EXAMPLE 4 (Comparative Example)

An antifreeze formulation was prepared comprising a major amount of ethylene glycol, 3.0 weight percent PTBBA, and 0.2 weight percent TTZ.

EXAMPLE 5

An antifreeze formulation was prepared comprising a major amount of ethylene glycol, 0.5 weight percent OA, 2.5 weight percent PTBBA, and 0.2 weight percent TTZ.

EXAMPLE 6

An antifreeze formulation was prepared comprising a major amount of ethylene glycol, 1.0 weight percent OA, 2.0 weight percent PTBBA, and 0.2 weight percent TTZ.

EXAMPLE 7

An antifreeze formulation was prepared comprising a major amount of ethylene glycol, 1.5 weight percent OA, 1.5 weight percent PTBBA, and 0.2 weight percent TTZ.

EXAMPLE 8

An antifreeze formulation was prepared comprising a major amount of ethylene glycol, 2.0 weight percent OA, 1.0 weight percent PTBBA, and 0.2 weight percent TTZ.

EXAMPLE 9

An antifreeze formulation was prepared comprising a major amount of ethylene glycol, 2.5 weight percent OA, 0.5 weight percent PTBBA, and 0.2 weight percent TTZ.

EXAMPLE 10

An antifreeze formulation was prepared comprising a major amount of ethylene glycol, 1.5 weight percent OA, 1.5 weight percent PTBBA, 1.3 weight percent borax, and 0.2 weight percent TTZ.

EXAMPLE 11

An antifreeze formulation was prepared comprising a major amount of ethylene glycol, 1.5 weight percent OA, 1.5 weight percent PTBBA, 0.1 weight percent sodium metasilicate pentahydrate, and 0.2 weight percent TTZ.

EXAMPLE 12

An antifreeze formulation was prepared comprising a major amount of ethylene glycol, 2.0 weight percent OA, 0.5 weight percent PTBBA, 0.5 weight percent SA, and 0.2 weight percent TTZ.

EXAMPLE 13

An antifreeze formulation was prepared comprising a major amount of ethylene glycol, 2.0 weight percent EHA, 1.5 weight percent PTBBA, and 0.2 weight percent TTZ.

EXAMPLE 14

An antifreeze formulation was prepared comprising a major amount of ethylene glycol, 2.0 weight percent EHA, 0.5 weight percent PTBBA, 1.5 weight percent borax, 0.1 weight percent sodium metasilicate pentahydrate, and 0.2 weight percent TTZ.

EXAMPLE 15

An antifreeze formulation was prepared comprising a major amount of ethylene glycol, 2.0 weight percent EHA, 0.5 weight percent PTBBA, 1.5 weight percent borax, 0.1 weight percent sodium metasilicate pentahydrate, 0.1 weight percent sodium nitrate, and 0.2 weight percent TTZ.

EXAMPLE 16

An antifreeze formulation was prepared comprising a major amount of ethylene glycol, 2.0 weight percent EHA, 0.5 weight percent PTBBA, 1.5 weight percent borax, 0.1 weight percent sodium metasilicate pentrahydrate, 0.1 weight percent sodium nitrite, and 0.2 weight percent TTZ.

It is well known that the corrosion resistance of a metal or alloy depends upon both the stability of its passivating oxide protective film and its ability to repassivate active corrosion regions on the surface of the metal or alloy. A Rapid Cyclic Potentiokinetic Polarization Scanning (RCP) technique, based on cyclic potentiokinetic polarization and described in the CEBELCOR (Centre Belge d'Etude de la Corrosion) publication Rapports Techniques, Vol. 147, R. T. 272 (Aug. 1984), may be used to determine the susceptibility of a metal or alloy to localized corrosion. The RCP technique measures both rupture or pitting potential (E_R) and repassivation potential (E_P) for a given metal or alloy. E_R is the potential at which the passivating film of a given material breaks down, and is directly related to the pitting tendency of the material in a particular environment. E_P is the potential at which active corrosion regions of the material are repassivated in a given environment. E_R and E_P values are measured with a silver reference electrode and a working electrode constructed from the material subject to corrosive attack. The higher (more positive) the E_R value, the more effective a given antifreeze formulation is in preventing pitting corrosion initiation and progress. Similarly, a higher (more positive) E_P value indicates that the particular corrosion inhibitor formulation has a greater ability to repassivate existing pits and crevices.

The RCP test procedure may be described as follows: polished specimens of the metal to be tested (working electrode) are immersed in a 30% by volume solution of a given antifreeze concentrate formulation in hard ASTM corrosive water; that is, water containing 148 mg/l of sodium sulfate, 165 mg/l of sodium chloride, 138 mg/l of sodium bicarbonate (ASTM D1384 corrosive water), and in addition 275 mg/l of calcium chloride.

Polarization is achieved by polarizing at a scan rate of 2 mv/second until rupture potential E_R is attained. A rapid increase in polarizing current results at E_R as the protective passivating film breaks down. When the current reaches a predetermined maximum value, the scanning direction is reversed towards more cathodic potentials. The repassivation potential E_P is determined during this final phase of the RCP scan.

Table I sets forth E_R and E_P values obtained via the RCP technique for Examples 1, 2, 3 and 7. Electrode potentials are shown for various metals for a borax-benzoate type corrosion inhibitor (Example 1), a dibasic acid corrosion inhibitor (Example 2), a monobasic-dibasic acid corrosion inhibitor (Example 3), and a corrosion inhibitor of the instant invention (Example 7). Significantly improved corrosion protection against pitting and crevice corrosion is shown, particularly for aluminum, magnesium, and lead. In addition, levels of copper, solder, and steel protection are reached by the instant invention which are equal to those of dibasic or monobasic-dibasic inhibitors.

The synergism in corrosion protection for the various metals in coolant soultions according to the instant invention is shown in Table II. E_R and E_P values obtained via the RCP technique for Examples 4, 5, 6, 7, 8, and 9 are shown for various metals in coolant solutions containing different amounts of PTBBA and OA.

Further improved corrosion protection for various metals is illustrated in Table III showing E_R and E_P values in coolant solutions containing PTBBA and OA, with additional amounts of borax (Example 10), sodium silicate (Example 11), and in coolants containing OA, PTBBA, & SA (Example 12), and EHA & PTBBA (Example 13).

The corrosion behavior of several of the formulations of the instant invention as well as comparative examples were tested according to the ASTM D-1384 Glassware Corrosion Test, incorporated herein by reference. Table IV sets forth the results obtained. The smaller the weight loss of the metal coupon, the greater the corrosion inhibiting properties of a particular formulation. A negative weight loss signifies a weight increase due to the formation of a protective coating on the coupon. As illustrated by Table IV, the antifreeze formulations of the instant invention (Examples 7, 12-16) provide corrosion protection for the metals tested comparable so that of the comparative examples tested (Examples 1-3).

TABLE I

RCP MEASUREMENTS TO DETERMINE CORROSION INHIBITOR EFFECTIVENESS (E_R AND E_P IN mv).

EXAMPLE	ALUMINUM		COPPER		SOLDER		STEEL		MAGNESIUM		LEAD	
	E_R	E_P	E_R	E_P	E_R	E_P	E_R	E_P	E_R	E_P	E_R	E_P
1	300	-400	750	100	200	-250	600	-500	-1700	-1650	1000	800
2	350	-600	1800	3000	1150	1100	650	620	-1500	-1400	1250	1100
3	720	-580	1850	1600	1200	1150	740	720	400	*	1100	1000
7	> 2400	*	1680	1500	1200	900	640	600	> 2000	> 2000	1450	2500

(All columns under the spanning heading WORKING ELECTRODE.)

* Repassivation potential E_P could not be determined.

TABLE II

RCP MEASUREMENTS DEMONSTRATING THE SYNERGISTIC EFFECT OF THE INSTANT INVENTION

WORKING ELECTRODE

EXAMPLE	ALUMINUM		COPPER		SOLDER		STEEL	
	E_R	E_P	E_R	E_P	E_R	E_P	E_R	E_P
4	1700	0	1900	320	1400	150	1150	1250
5	2300	100	1880	100	1450	1600	760	1200
6	> 2400	*	2100	100	1600	1800	740	720
7	> 2400	*	1680	1500	1200	900	640	600
8	> 2400	510	1600	1500	1260	980	700	650
9	> 2400	1400	1540	100	1200	900	700	680

* Repassivation potential E_P could not be determined.

TABLE III

RCP MEASUREMENTS DEMONSTRATING THE EFFECTIVENESS OF DIFFERENT COMBINATIONS OF THE CORROSION INHIBITOR OF THE INSTANT INVENTION

WORKING ELECTRODE

EXAMPLE	ALUMINUM		COPPER		SOLDER		STEEL	
	E_R	E_P	E_R	E_P	E_R	E_P	E_R	E_P
10	> 2400	*	2000	> 2400	1400	1450	750	740
11	2350	1500	1200	220	1400	1500	740	760
12	> 2400	1100	1980	1830	1400	1150	700	670
13	2350	950	2125	950	1400	1000	700	700

* Repassivation potential E_P could not be determined.

TABLE IV

RESULTS OF ASTM D1384 GLASSWARE CORROSION TESTS

GLASSWARE CORROSION TEST
(weight loss,mg/coupon)

EXAMPLE	Copper	Solder	Brass	Steel	Iron	Aluminum
1	1.7	4.6	1.0	2.2	6.2	-0.8
2	1.1	1.2	0.2	1.1	0.4	6.6
3	1.2	1.7	1.4	1.4	0.7	- 0.3
7	1.6	1.3	1.6	-0.3	-0.3	0.3
12	2.2	2.8	1.5	0	2.7	3.2
13	2.5	2.7	1.8	0.2	1.8	2.6
14	1.2	0.9	-1.1	- 0.1	1.6	2.0
15	0.4	1.4	0.8	0.3	2.4	2.5
16	0.8	1.5	0.8	- 0.2	2.7	1.7

Claims

1. A corrosion-inhibited antifreeze concentrate composition comprising from 90-99 wt % of a water soluble liquid alcohol freezing point depressant;
characterised by

a) from 0.1 - 5.0 wt % of an alkylbenzoic acid or an alkali metal, ammonium, or amine salt thereof, said acid having the general formula

where R is a C_1 - C_5 alkyl radical;

b) from 0.1 - 5.0 wt % of a C_8 - C_{12} aliphatic monobasic acid or an alkali metal, ammonium, or amine salt thereof; and

c) from 0.1 - 0.5 wt % of a hydrocarbyl triazole.

2. A corrosion-inhibited antifreeze concentrate composition of Claim 1 characterised in that said alkyl benzoic acid is 4-tert-butylbenzoic acid.

3. A corrosion-inhibited antifreeze concentrate composition of either preceding Claim characterised in that the C_8 - C_{12} aliphatic monobasic acid is selected from octanoic acid, nonanoic acid, decanoic acid, undecanoic acid, dodecanoic acid, 2-ethylhexanoic acid, and neodecanoic acid.

4. A corrosion-inhibited antifreeze concentrate composition of any preceding Claim characterised in that said hydrocarbyl triazole is tolyltriazole or benzotriazole, and is present in a concentration of 0.1 - 0.3 wt %.

5. A corrosion-inhibited antifreeze concentrate composition of any preceding Claim, characterised in that a C_8 - C_{12} aliphatic dibasic acid corrosion inhibitor or the alkali metal, ammonium, or amine salt thereof is additionally employed in a concentration of 0.1 - 5.0 wt %.

6. A corrosion-inhibited antifreeze concentrate composition of Claim 5, characterised in that said C_8 - C_{12} aliphatic dibasic acid is selected from suberic acid, azelaic acid, sebacic acid, undecanedioic acid, dodecanedioic acid, and the diacid of dicyclopentadiene.

7. A corrosion-inhibited antifreeze concentrate composition of any preceding Claim characterised in that an additional corrosion inhibitor selected from alkali metal borates, alkali metal silicates, alkali metal benzoates, alkali metal nitrates, alkali metal nitrites, alkali metal molybdates, and hydrocarbyl thiazoles is also employed at a concentration of 0.01 - 5.0 wt %.

8. A corrosion-inhibited antifreeze concentrate composition of any of Claims 1 to 7 characterised in that said antifreeze composition is diluted with from 10 - 90 volume percent of water.

9. A process for inhibiting the corrosion of metals present in the cooling system of an internal combustion engine which comprises intimately contacting the metal surface to be inhibited against corrosion with the corrosion-inhibited antifreeze composition of Claim 8.

Patentansprüche

1. Korrosionsinhibierte Zusammensetzung zur Verwendung als Gefrierschutzkonzentrat, die 90 - 99 Gew.-% eines Gefrierpunktserniedrigungsmittels auf der Basis eines wasserlöslichen flüssigen Alkohols umfaßt;
gekennzeichnet durch

a) 0,1 - 5,0 Gew.-% einer Alkylbenzoesäure oder eines Alkalimetall-, Ammonium- oder Amin-Salzes derselben, wobei besagte Säure die allgemeine Formel besitzt

in der R ein C_1-C_5-Alkylrest ist;

b) 0,1 -5,0 Gew.-% einer einbasigen aliphatischen C_8-C_{12}-Säure oder eines Alkalimetall-, Ammonium- oder Amin-Salzes derselben; und

c) 0,1 - 0,5 Gew.-% eines Kohlenwasserstofftriazols.

2. Korrosionsinhibierte Zusammensetzung zur Verwendung als Gefrierschutzkonzentrat nach Anspruch 1, dadurch gekennzeichnet, daß besagte Alkylbenzoesäure 4-tert.-Butylbenzoesäure ist.

3. Korrosionsinhibierte Zusammensetzung zur Verwendung als Gefrierschutzmittel nach einem der vorangehenden Ansprüche, dadurch gekennzeichnet, daß die einbasige aliphatische C8-C_{12}-Säure ausgewählt ist aus Oktansäure, Nonansäure, Dekansäure, Undekansäure, Dodekansäure, 2-Ethylhexansäure und Neodekansäure.

4. Korrosionsinhibierte Zusammensetzung zur Verwendung als Gefrierschutzkonzentrat nach einem der vorangehenden Ansprüche, dadurch gekennzeichnet, daß besagtes Kohlenwasserstofftriazol Tolyltriazol oder Benzotriazol ist und in einer Konzentration von 0,1 - O,3 Gew.-% vorliegt.

5. Korrosionsinhibierte Zusammensetzung zur Verwendung als Gefrierschutzkonzentrat nach einem der vorangehenden Ansprüche, dadurch gekennzeichnet, daß ein Korrosionsinhibitor auf der Basis einer zweibasigen aliphatischen C_8-C_{12}-Säure oder das Alkalimetall-, Ammonium- oder Amin-Salz desselben zusätzlich in einer Konzentration von 0,1 - 5,0 Gew.-% eingesetzt wird.

6. Korrosionsinhibierte Zusammensetzung zur Verwendung als Gefrierschutzkonzentrat nach Anspruch 5, dadurch gekennzeichnet, daß besagte zweibasige aliphatische C_8-C_{12}-Säure ausgewählt ist aus Suberinsäure, Azelainsäure, Sebacinsäure, Undekandisäure, Dodecandisäure und dem Diacid von Dicyclopentadien.

7. Korrosionsinhibierte Zusammensetzung zur Verwendung als Gefrierschutzkonzentrat nach einem der vorangehenden Ansprüche, dadurch gekennzeichnet, daß ein zusätzlicher Korrosionsinhibitor, ausgewählt aus Alkalimetallboraten, Alkalimetallsilikaten, Alkalimetallbenzoaten, Alkalimetallnitraten, Alkalimetallnitriten, Alkalimetallmolybdaten und Kohlenwasserstoffthiazolen in einer Konzentration von 0,01 - 0,5 Gew.-% ebenfalls eingesetzt wird.

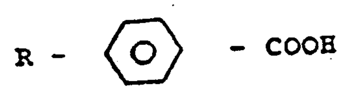
8. Korrosionsinhibierte Zusammensetzung zur Verwendung als Gefrierschutzkonzentrat nach einem der Ansprüche 1 bis 7, dadurch gekennzeichnet, daß besagte Gefrierschutzzusammensetzung mit 10 - 90 Vol.-% Wasser verdünnt ist.

9. Verfahren zum Inhibieren der Korrosion von Metallen, die im Kühlsystem eines Verbrennungsmotors vorhanden sind, welches das innige In-Kontakt-Bringen der gegen Korrosion zu inhibierenden Metalloberfläche mit der korrosionsinhibierten Gefrierschutzzusammensetzung von Anspruch 8 umfaßt.

Revendications

1. Composition concentrée antigel et anticorrosion, comprenant de 90 à 99 % en poids d'un agent liquide d'abaissement du point de congélation soluble dans l'eau à base d'alcool ;
caractérisée en ce qu'elle comprend :

a) de 0,1 à 5,0 % en poids d'un acide alkylbenzoïque ou d'un sel de celui-ci avec un métal alcalin, un ion ammonium ou une amine, cet acide répondant à la formule générale :



dans laquelle R représente un groupe alkyle en C_1-C_5 ;

b) de 0,1 à 5,0 % en poids d'un monoacide aliphatique en C_8 à C_{12}, ou d'un sel de celui-ci avec un métal alcalin, un ion ammonium ou une amine ; et

c) de 0, 1 à 0, 5 % en poids d'un hydrocarbyl triazole.

2. Composition concentrée antigel et anticorrosion selon la revendication 1, caractérisée en ce que l'acide alkylbenzoïque est l'acide 4-tert-butylbenzoïque.

3. Composition concentrée antigel et anticorrosion selon l'une quelconque des revendications précédentes, caractérisée en ce que le monoacide aliphatique en C_8 à C_{12} est choisi parmi l'acide octanoïque, l'acide nonanoïque, l'acide décanoïque, l'acide undécanoïque, l'acide dodécanoïque, l'acide 2-éthylhexanoïque et l'acide néodécanoïque.

4. Composition concentrée antigel et anticorrosion selon l'une quelconque des revendications précédentes, caractérisée en ce que l'hydrocarbyl triazole est le tolyltriazole ou le benzotriazole, et en ce qu'il est présent selon une concentration de 0,1 à 0,3 % en poids.

5. Composition concentrée antigel et anticorrosion selon l'une quelconque des revendications précédentes, caractérisée en ce que l'on emploie en outre, un inhibiteur de corrosion à base d'un diacide aliphatique

en C_8 à C_{12} ou d'un sel de celui-ci avec un métal alcalin, un ion ammonium ou une amine, selon une concentration de 0,1 à 5,0 % en poids.

6. Composition concentrée antigel ou anticorrosion selon la revendication 5, caractérisée en ce que le diacide aliphatique en C_8 à C_{12} est choisi parmi l'acide subérique, l'acide azélaïque, l'acide sébacique, l'acide undécanedioïque, l'acide dodécanedioïque, et le diacide dérivé du dicyclopentadiène.

7. Composition concentrée antigel et anticorrosion selon l'une quelconque des revendications précédentes, caractérisée en ce que l'on emploie également selon une concentration de 0,01 à 5,0 % en poids, un inhibiteur de corrosion supplémentaire choisi parmi les borates de métal alcalin, les silicates de métal alcalin, les benzoates de métal alcalin, les nitrates de métal alcalin, les nitrites de métal alcalin, les molybdates de métal alcalin et les hydrocarbyl thiazoles.

8. Composition concentrée antigel et anticorrosion selon l'une quelconque des revendications 1 à 7, caractérisée en ce que la composition antigel est diluée dans 10 à 90 % en volume d'eau.

9. Procédé d'inhibition de la corrosion de métaux présents dans le système de refroidissement d'un moteur à combustion interne, selon lequel on met en contact intime la surface métallique destinée à être protégée contre la corrosion, avec la composition antigel et anticorrosion de la revendication 8.